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Quantum Theory of Chemical Reaction Rates

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Project Director

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Abstract

We examine the rate constants of chemical exchange reactions involving relatively light atoms. Such reactions have specific quantum characteristics, so that the usual classical statistical theory of chemical reaction rates is not applicable. We show how one can set about calculating reaction rates for such processes. At present the limitation to quantitative calculations lies in our inadequate knowledge of interatomic potential energy functions.

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1. Introduction

We shall discuss the rate constant for a simple bimolecular reaction -

(1) $$AB + C \rightarrow A + BC,$$

where A,B, C are atoms or molecules. The rate constant for this reaction will in general be given by an expression of the form

(2) $$k_{fo}(T) = P_{fo} Z\, e^{-E_{act}/kT},$$

where Z is the number of collisions of AB and C per second ($\sim 10^{9\text{-}13}$, or less depending on density); it is defined in terms of an effective molecular radius and thus is clearly not a very precise concept. E_{act} ($\sim$ 5-50 Kcal/mole, i.e., 0.2-2 ev) is the 'activation energy', and P_{fo} ($\sim 10^{-3}$ -1) a 'steric factor'. Both P_{fo} and Z will be mildly temperature dependent, but the principal - and very striking - temperature variation of the rate constant arises from the activation energy. The problem is thus to explain the character of the expression (2) for the rate constant.

The standard interpretation of (2) is that there must exist an 'activated state' (ABC), whose energy is E_{act} above that of AB + C at infinite separation. We say that this state must be formed if there is to be a reaction (1). Once the state has been formed it will have some definite (statistical) life time, after which it can presumably break up into AB + C or into A + BC, both of which will in general be energetically accessible from (ABC).

Thus the reaction (1) should really be written

(3) $$AB + C \xrightarrow[k_{jo}]{} (ABC)$$

(4) $$(ABC) \xrightarrow[k_{oj}]{} AB + C$$

(5) $$(ABC) \xrightarrow[k_{fj}]{} A + BC$$

where we use the index o for the state AB + C, j for (ABC), and f for A + BC.

Let us now ask whether the interpretation (3-5) is in fact a necessary consequence of the expression (2) for the rate. The answer seems quite definitely to be yes. For, consider how an expression like (2) is arrived at. Suppose that a molecule AB and an atom C in given internal states collide with relative velocity v_o. Then we calculate the transition probability $k_{fo}(v_o) = v_o \sigma_{fo}(v_o)$, where σ_{fo} is the reaction cross section. From this we get the temperature-averaged transition rate $k_{fo}(T)$ by averaging $k_{fo}(v_o)$ over a Maxwell distribution in v_o:

$$(6) \qquad k_{fo}(T) = (\text{const.}) \times \int k_{fo}(v_o) \exp\left[-M_e v_o^2/2kT\right] v_o^2 \, dv_o .$$

Now the question is, how can we get an expression of type (2) from (6); and the answer is that if $k_{fo}(v_o)$ or $\sigma_{fo}(v_o)$ are reasonable functions, then essentially the only possibility is that these functions must vanish for

$$(7) \qquad v_o < \sqrt{2E_{act}/M_e} \quad .$$

This clearly indicates that E_{act} represents some kind of threshold below which no reaction can take place. The threshold presumably refers to some quantum state of the three atoms A, B, C (since it is not an eigenstate of the separate systems), and this state is customarily called the activated state (ABC). It is clear that while (ABC) is a perfectly definite state (as this argument shows), yet its life time is not very long, because it is not observed directly by normal chemical techniques.

There are a number of steps involved in calculating the rate constant of a process of type (1) namely:

(i) Analyze the character of the activated state (ABC).

(ii) Calculate the transition rate $k_{jo}(v_o)$ of the process (3).

(iii) Make some kind of estimate of the probability p_{fj} of the activated state

breaking up in the manner (5) rather than (4),

$$p_{fj} = k_{fj} / (k_{fj} + k_{oj}). \tag{8}$$

(iv) Finally, carry out the temperature average (6).

Of these steps, (iv) is a trivial technical matter once the rest of the work has been done; (iii) is not difficult in principle, once we have solved step (ii) - though in practice we shall use a short-cut (cf. Section 5). This brings us to the major problems (i) and (ii).

The activated state has been analyzed by Pelzer and Wigner, London, Polanyi, Eyring and others [1,2]. These authors have shown that if one regards the nuclei as at rest in the field of the orbital electrons, and calculates the total energy of the electrons quantum-mechanically for various positions of the nuclei (Born-Oppenheimer adiabatic separation), then one obtains the potential energy diagram of Figure 1 with a saddle point between the asymptotic valleys o (= AB + C) and f (= A + BC).[N.1] The state j = (ABC) is regarded classically as a state located on or about the saddle point.

The problem was taken up quantum-mechanically by Bauer and Wu [3], who followed a suggestion of Mott and Massey [4]. The state (ABC) is regarded as vibrationally excited, which is reasonable in view of its character involving nuclear motion, and of the order of magnitude of the energy of excitation,

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N.1 In Figure 1, as in most of the classical calculations and in the present considerations, we have assumed that the three atoms A, B, C lie in one straight line throughout their collision. If one tried to consider glancing collisions and rotational motion, the 'potential energy surface' of Figure 1 and Section 3 would have to be replaced by a six-dimensional hypersurface. Some effects that would occur if one tried to discuss rotational motion are mentioned in Section 8.

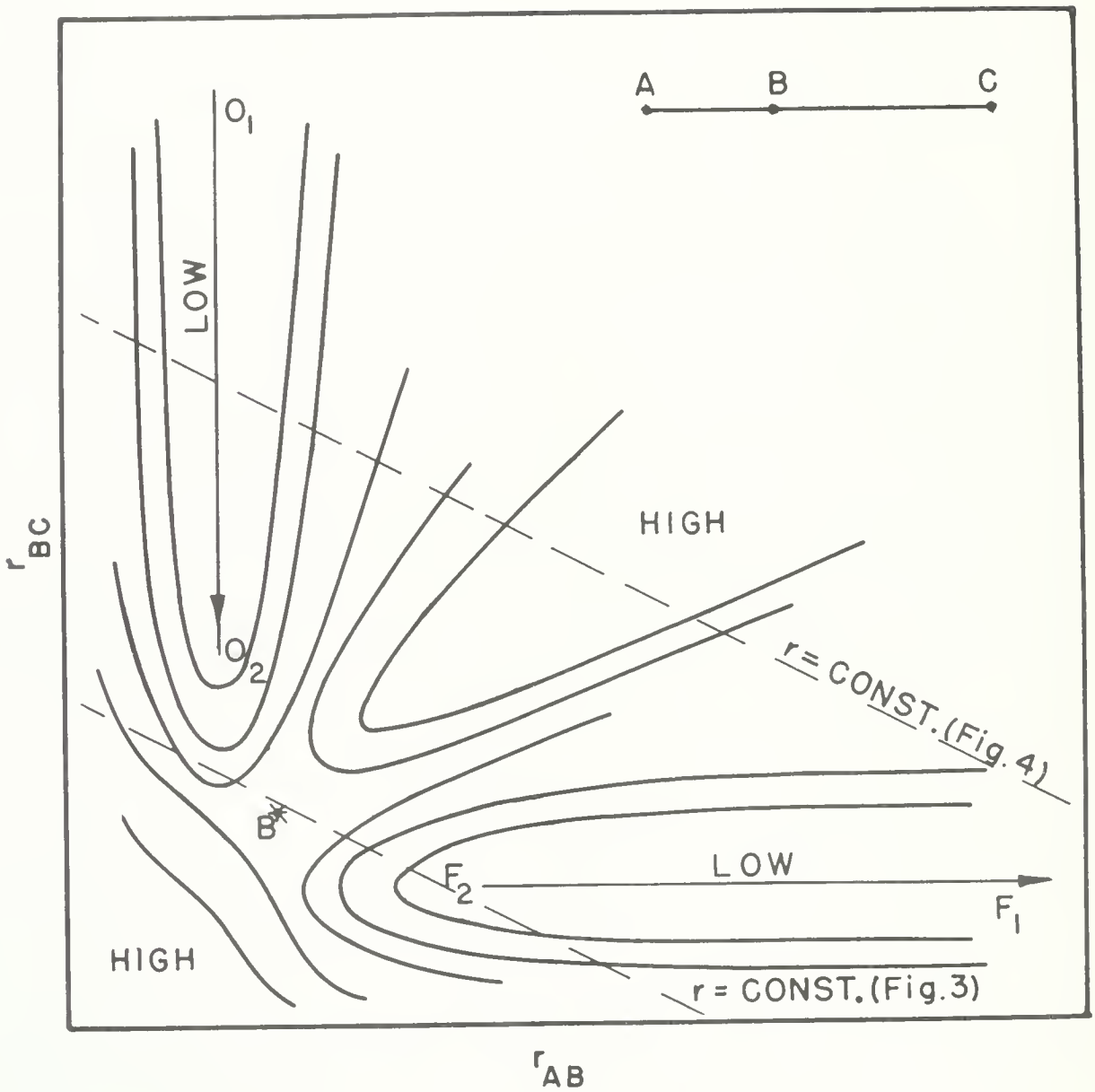

FIGURE 1

Potential energy surface of a collinear system A-B-C, in terms of the coordinates r_{AB} and r_{BC}. The arrows indicate the approach of C towards AB and the final separation of A from BC. B* is the saddle point of the surface.

E_{act} [N.2]. Now, evidently a state of this kind has to be treated quantum-mechanically provided its vibrational quantum number is low (of order 1, not 10). In fact for interactions of light atoms the vibrational quantum number is low[3], and thus we have an immediate reason why the statistical treatments[1,2], which treat the activated state classically, cannot be regarded as a satisfactory approximation. In fact there are very serious difficulties in attempting a detailed quantum-mechanical calculation, but now one can at least analyze them. Let me remark that at present the essential limitation lies in the inadequacy of presently available quantum-mechanical calculations of potential energy surfaces. This will be discussed in more detail in Section 3.

The final point is (ii), the calculation of the transition rate $k_{jo}(v_o)$. Here there is very definite progress to report over the early work[3]. If we treat the activated state as vibrationally excited, then recent calculations[5,6,7] enable us in principle to make proper quantum-mechnical calculations of the rate constant which are essentially limited only by our inadequate knowledge of the potential energy surfaces.

It is clear that there is a strong qualitative similarity between the present problem and Bohr's compound nucleus theory, which describes the interaction of nucleons with relatively heavy nuclei. However, there is an essential quantitative difference in the quantum character of the activated state for groups of light atoms, and of the compound nucleus containing a fairly large number of nucleons ($N \gtrsim 25$). The compound nucleus has very many closely spaced excited

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[N.2] A characteristic energy for rotational degrees of freedom is $\sim .05$ ev, $\sim$ 0.2 - 0.5 ev for vibration; ~ 5 ev for electronic excitation. Energies of dissociation (a vibrational type process) are of order 3 ev, while ionization potentials are ~ 10 ev.

states, any or all of which can be occupied, so that the ensemble can be treated statistically or 'classically'. In the present case the activated state has very few quantum states, and must therefore be treated by quantum mechanics [N.3].

2. Formulation

To discuss the problem further, we must give a proper formulation. In the statistical theory it is customary to use the coordinates $\vec{r}_{AB}$ and $\vec{r}_{BC}$, but in a quantum-mechanical calculation we wish to eliminate the motion of the center of mass, and also to write the kinetic energy as the sum of squares of momenta, without any cross terms. To achieve this, we use the coordinates [8]

$$(9)\qquad \begin{cases} \vec{\rho} = \vec{r}_{AB} \\ \vec{r} = \vec{r}_C - (M_A \vec{r}_A + M_B \vec{r}_B)/(M_A + M_B) \\ \vec{R} = (M_A \vec{r}_A + M_B \vec{r}_B + M_C \vec{r}_C)/(M_A + M_B + M_C) \end{cases}$$

for which we write the quantum hamiltonian as

$$(10)\qquad \begin{cases} (a) \quad H = H_i^o + H_e^o + H_T^o + V'(\vec{\rho},\vec{r}) \\ (b) \quad H_i^o = (-\hbar^2/2M_i)\nabla^2_{\vec{\rho}} + V_i^o(\vec{\rho});\ M_i = M_A M_B/(M_A+M_B) \\ (c) \quad H_e^o = (-\hbar^2/2M_e)\nabla^2_{\vec{r}} + V_e^o(\vec{r});\ M_e = M_C(M_A+M_B)/(M_A+M_B+M_C). \end{cases}$$

N.3 If one considers glancing collisions, i.e., rotational fine structure, there will be many more states than in the present discussion. However, the selection rules for rotational transitions (cf. Section 8) indicate that for a single transition process the situation will be essentially as outlined here, although the potential energy curves will be slightly different for different values of angular momentum.

$H_T^o = H_T^o(\vec{R})$ gives only the motion of the center of mass, which does not affect the cross section. It is omitted, and thus conservation of linear momentum is automatically ensured and does not have to be considered in the following. Of the two remaining coordinates, $\vec{\rho}$ describes the internal motion of the molecule AB, ('i' for internal), while $\vec{r}$ represents the external ('e') motion of C relative to AB.

Now we wish to solve the quantum-mechanical problem

$$(11) \qquad (H_i^o + H_e^o + V' - E)\, \underline{\Psi}_n(\vec{\rho},\vec{r}) = 0; \qquad n = o,j,f.$$

In fact, we shall solve the problem by perturbation theory, basing the discussion on eigenfunctions of the uncoupled hamiltonian $(H_i^o + H_e^o)$ [3],

$$(12) \quad \begin{cases} (a) \quad (H_i^o + H_e^o - E)\, \underline{\Phi}_n(\vec{\rho},\vec{r}) = 0. \\ (b) \quad \underline{\Phi}_n(\vec{\rho},\vec{r}) = \phi_n(\vec{\rho})\psi_n(\vec{r}) \\ (c) \quad (H_i^o - \epsilon_n)\phi_n(\vec{\rho}) = 0 \\ (d) \quad \psi_n(\vec{r}) = \sum_{\ell=o}^{\infty} \chi_\ell(k_n r) P_\ell(\cos\theta_n)/r \\ (e) \quad \left[d^2/dr^2 + \ell(\ell+1)/r^2 - (2M_e/\hbar^2)V_e^o(r) + k_n^2\right] \chi_\ell(k_n r) = 0 \quad \text{N.4} \\ (f) \quad \chi_\ell(k_n r) \sim \cos(k_n r + \delta_{n,\ell}) \quad \text{as } r \to \infty . \end{cases}$$

Conservation of energy and angular momentum between two states n, n' gives the conditions

$$(13) \qquad E = (\hbar^2 k_n^2 / 2M_e) + \epsilon_n = (\hbar^2 k_{n'}^2/2M_e) + \epsilon_{n'} ,$$

$$(14) \qquad \ell_n = \ell_{n'} .$$

N.4 Note that in writing (12e) we have assumed $V_e^o(\vec{r}) = V_e^o(|\vec{r}|) = V_e^o(r)$. If this is not so, one should write $V_e^o(\vec{r}) = \sum_{m=o}^{\infty} V_{e,m}^o(r) P_m(\cos\theta_n)$, and proceed from there.

The transition probability per unit time is given by

$$(15) \qquad k_{n',n} = \frac{2\pi}{\hbar} \left| (\bar{\Phi}_{n'}, V' \bar{\Phi}_{n}) \right|^2 d\rho/dE_{(n')} ,$$

where $d\rho/dE_{(n')}$ gives the density of final states per unit energy range.

We are here setting up the problem in terms of quantum-mechanical perturbation theory. The use of quantum theory here is of course distinct from its use in describing the activated state, but in fact a quantum treatment is again necessary[5]; this point is discussed in detail in Section 6. One could of course solve the classical problem corresponding to (9) - (15), although a considerable reformulation would be necessary.

Regarding the use of perturbation theory, this is essentially unavoidable. Even in classical mechanics, the three-body problem cannot be solved exactly, in general, and thus we can hardly expect to do any better in quantum theory. Some earlier quantum calculations of the excitation of molecular vibration by collisions talk about using 'distorted wave' or 'perturbed stationary state' methods; these are not exact, but somewhat better in principle than straight perturbation theory. However, when it comes to the point, everybody uses some form of perturbation theory. There is one serious difficulty in principle which can be important in certain energy ranges. The scattering matrix is not unitary in perturbation theory, so that the calculated transition probabilities do not satisfy flux conservation unless $|(\bar{\Phi}_{n'}, V' \bar{\Phi}_{n})|$ is small in some appropriate sense.[N.5]

[N.5] This problem is not likely to arise in the present application at reasonable energies, but it will enter into discussions of three-body recombination where we are dealing with relatively small energy transfer and consequently large transition probabilities. Work on this problem is being done (in different contexts) by J. Keck at AVCO and by M. Salkoff at New York University.

Before we go any further, we have to examine the potential energy in detail. It is known [9] that the cross section is an exceedingly sensitive function of the potential, and thus we shall examine the problem of obtaining an expression for the potential energy, and of separating V', from V_i^o and V_e^o. This problem is discussed in Section 3. In the following sections we shall examine the kind of model for the activated state[N.1] used in the statistical theory [1,2] and in the earlier quantum mechanical work [3].

3. Difficulties in calculating the potential energy

It is quite clear in principle how one sets about calculating the potential energy function which determines the motion of the nuclei in the 'smeared-out' field of the orbital electrons. One makes a quantum-mechanical calculation of the energy of the electrons moving in the field of the stationary nuclei. By making this calculation for a variety of (fixed) positions of the nuclei, one obtains an energy function which determines the interaction of the heavy particles with one another. In particular, if one considers the three nuclei A, B, C as moving in a straight line, then the potential energy function will be the usual 'potential energy surface' [N.1,6].

The difficulties in carrying out this program are 'merely' technical, but they are exceedingly formidable on account of the large number of electrons involved. For instance, for the cases

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[N.6] If we consider several electronic states of the system as a whole, then each will have its own potential energy function or surface. We just consider the lowest of this manifold of surfaces, disregarding electronic excitation. This is justified by the adiabatic hypothesis; in practice it is very satisfactory if we restrict ourselves to temperatures below about 5000°K.

$$(16)\quad \begin{cases} \text{(a)}\ \ H_2 + F \longrightarrow HF + H \\ \text{(b)}\ \ N_2 + O \longrightarrow NO + N \end{cases}$$

there are respectively 11 and 22 orbital electrons, giving three times this number of degrees of freedom; even with the simplification of considering only electrons in the outermost unfilled sub-shell in each case, we still have 9 and 11 electrons respectively. An actual solution of the wave equation for such a system by either analytic or numerical means seems to be out of the question with presently available techniques, and thus one is reduced to using variational techniques [10,11].

The accuracy required is of the order of thermal energies, i.e.,.03 ev, as compared with molecular binding energies of the order of 3 ev. Such accuracy is exceedingly difficult to obtain; for the classic case of the ground state of the hydrogen molecule [11], which involves only two electrons, such orders of accuracy were only obtained with wave functions involving about 10 variational parameters. This may well be a somewhat unfavorable example, and more recently developed techniques may cut down the number of variational parameters required per electron, but the problem is still very difficult. I believe that with modern high-speed computing equipment as fast as the IBM 704 or Remington Rand 1103, it would be possible to attempt the calculation of potential energy functions to this order of accuracy.

Thus the position is clear. At present it is not feasible to attempt to make quantitative calculations of reaction rates for even the simplest processes because we lack the quantitative knowledge of the potential energy functions necessary to ensure meaningful answers. However, we can give a qualitative analysis of the problem, discussing significant features and needed improvements, with the aim of showing how one can set about doing these calculations in principle.

4. The activated state in the classical statistical theory [1,2]

This is a brief review of the usual theory. In Figure 1 we have the potential energy surface N.1 in its customary form, in terms of the coordinates r_{AB} and r_{BC}. We consider the system moving along the initial track O_1 O_2 up to the saddle point B^* where it stays for a relatively long time because most of its energy has been converted from kinetic to potential energy, so that its velocity is very low, and hence it takes a long time to travel around on the saddle point. The region of the saddle point represents the activated state j, and its height above the valley floor at infinity (O_1) is the classical activation energy. The system stays in the activated state sufficiently long for it to 'forget' how it got there; eventually it goes either into the final state f or into the initial state o.

To calculate the rate, one defines a mean collision frequency $Z = Z(T)$ which indicates the number of times an AB molecule and a C atom come sufficiently close to one another (say to O_2) for there to be a reaction. Once it gets into this configuration, then the probability of the system getting up to the saddle will be proportional to the relative volume of phase space, or to the partition function of the system 'in' the saddle relative to that of the system along the O-asymptote. If the partition function for the system in state n (= o,j,f) is $f_n(T)$, then

$$p_{jo}^{class}(T) = f_j(T)/f_o(T), \tag{17}$$

while

$$p_{jo}^{class}(T) = p_{fj}^{class}(T)\, p_{jo}^{class}(T). \tag{18}$$

It is customary to write $p_{fj}^{class}(T)$ as simply an adjustable $\kappa \sim \frac{1}{2}$; this was also done in the earlier quantum calculation [3].

This is a brief outline of the theory. Many applications of it have been made; sometimes (2) is replaced by the equivalent expression

$$(19)\quad \begin{cases} (a)\quad k_{fo}(T) = Z(T)\exp\left[-F_{act}/kT\right] \\ (b)\quad F_{act} = E_{act} - T\,S_{act} \\ (c)\quad \exp(S_{act}/k) = P_{fo}. \end{cases}$$

F_{act} and S_{act} are called free energy and entropy of activation. This terminology is used in the 'absolute reaction rate theory', a version of the theory which describes reaction rates in terms of equilibrium thermodynamic concepts.

5. Quantum-mechanical model of the activated state [3]

First of all, let us redraw the potential energy surface of Figure 1 in terms of the coordinates (ρ,r) of (9). This is shown in Figure 2. To attempt to solve the motion of the system along a track $O_1\ O_2\ B^*\ F_2\ F_1$ would be very difficult even if we knew the orbit accurately, which we don't. Thus we make an important simplifying assumption to enable us to carry out the calculation.

Assumption:

We replace the actual system by a model in which the passage of the system (AB + C) during the approach of C from infinite separation to a configuration in which AB and C are very close together, takes place adiabatically, i.e., without quantum jumps; the quantum transition $0 \rightarrow j$ then takes place suddenly [12] in the immediate neighborhood of the configuration of close approach.

This assumption can be partly justified by the short range of the interaction potential responsible for the transition (1).

We see thus that the process of attaining the activated state j falls into two parts. First of all, during the adiabatic passage of the system from infinite to small separation, the zero-point vibrational energy of the molecule AB will change by a (presumably relatively small) amount E'_{act}; this energy is supplied

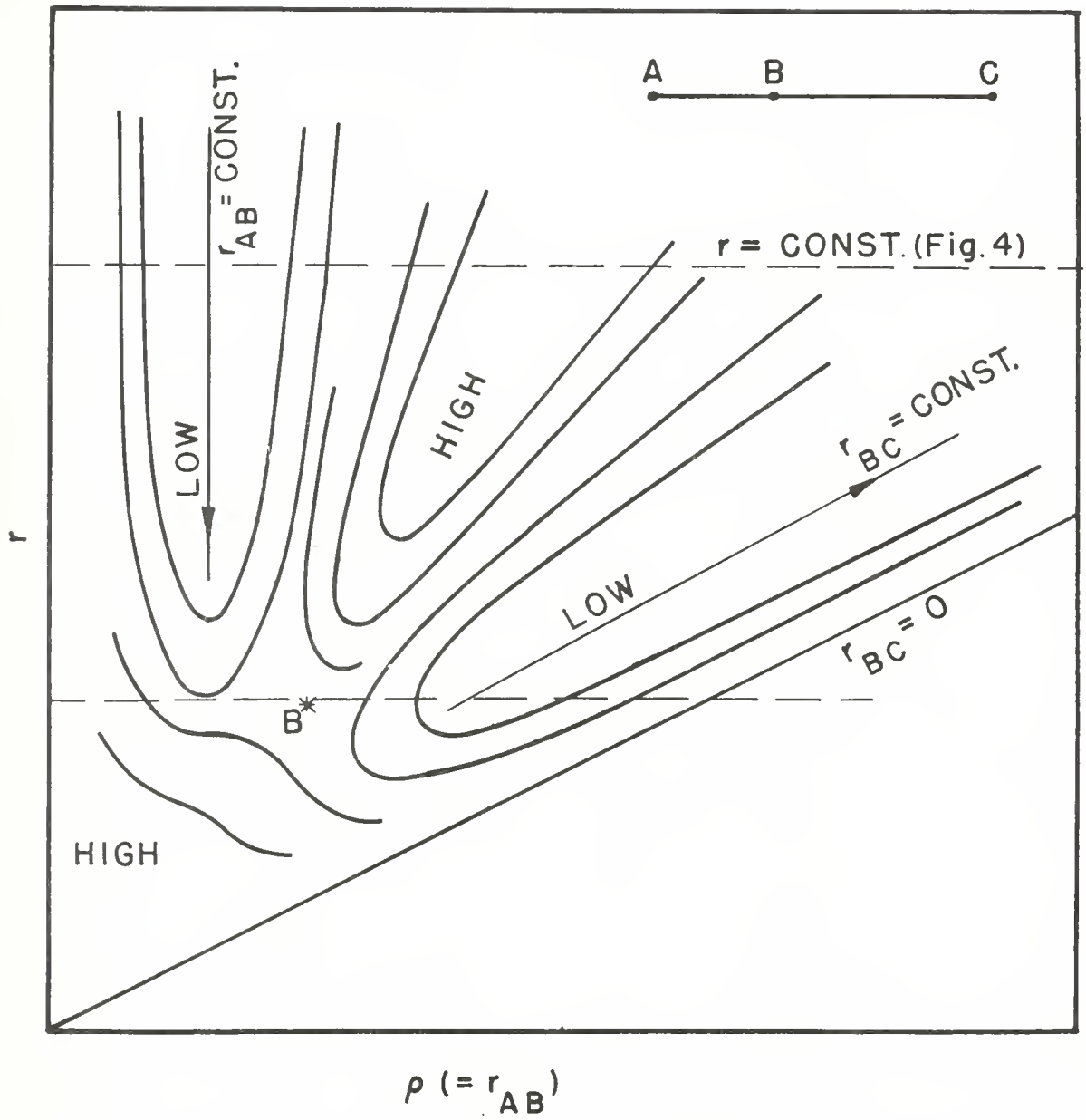

FIGURE 2

Potential energy surface in Fig. 1 in terms of the coordinates ρ, r defined by Eqs. (9). The arrows have the same meaning as in Fig. 1. The kinetic energy of relative motion (in the coordinate r) is assumed to be transformed into the vibrational motion of the system ABC (in the coordinate ρ), forming the excited state of the configuration near the saddle point B*.

from the relative kinetic energy of the system. Then, when the atom and molecule are very close together, the quantum jump from the ground vibrational state o to the excited state j will take place with a transfer E''_{act} of energy from kinetic into potential (vibrational) energy. Thus the total activation energy E_{act} is the sum of these two contributions, of which the second will in general be very much larger than the first[N.7]

$$(20)\quad \begin{cases} E_{act} = E'_{act} + E''_{act} \\ E'_{act} = \text{van der Waals' energy, } \sim .02 \text{ ev; } E''_{act} = \text{vibrational energy, } \sim .2 \text{ ev.} \end{cases}$$

In the light of this assumption, we can now break up the potential energy into $V^o + V'$ in such a way that a calculation can be made. We do this by expanding $V(\rho,r)$ about the value $V(\rho_J,r_J)$ at some point (ρ_J, r_J) which is characteristic of the configuration at the distance of closest approach of AB and C, and we then treat $(\rho-\rho_J)$ and $(r-r_J)$ as small [3]N.8 . Thus the total potential energy is

$$(21)\quad \begin{cases} (a)\quad V(\rho,r) = V_i^o(\rho,r_J) + V_e^o(\rho_J,r) + V'(\rho,r) \\ (b)\quad V'(\rho,r) = (\rho-\rho_J)\dfrac{\partial V_e(\rho_J,r)}{\partial \rho_J} + (r-r_J)\dfrac{\partial V_i^o(\rho,r_J)}{\partial r_J} + \text{---} \ . \end{cases}$$

We see that as ρ_J and r_J are constants, we have now formally carried out a separation of the hamiltonian into additive terms in $\vec{\rho}$ and in $\vec{r}$, which together form the unperturbed hamiltonian, and a perturbation V' which couples the ρ - and

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N.7 In our earlier calculations [3] we put $E'_{act} = 0$; the existence in principle of the term E'_{act} was pointed out to me by Dr. B. Widom.

N.8 Because the distances ρ_J and r_J are comparable, we cannot treat ρ and r in the unsymmetric way that is used in some problems [5,6,7].

$\vec{r}$-motions. This separation is meaningful in the sense of the assumption made above.

Let us now examine the potentials $V_i^o(\rho)$ and $V_e^o(r)$ more closely. The potential $V_e^o(r)$ is obtained in principle by taking a section through the potential energy surface of Figure 2 keeping $\rho = \rho_J$ = constant, i.e., roughly through the point B^*. It has the character of a van der Waals potential, being strongly repulsive for small r and weakly attractive for large r. The potential $V_i^o(\rho)$ is much more interesting. If we take a section through the point B^* of Figure 2, keeping $r = r_J$ = constant, we get a double minimum potential of the sort shown in Figure 3 [N.9].

The case where the potential energy function of Figure 3 is symmetrical with respect to inversion about the center point B^* has been examined rather thoroughly before; here we wish to examine the assymetric case qualitatively.

First of all, it is clear that Figure 3 is just one of a sequence of similar sections, for various values of r. A typical one for a very much greater value of r than r_J is shown in Figure 4. If we start with a molecule AB in its lowest vibrational state, then clearly we are in the vibrational state of Figures 3,4. We now ask how the system can go over from AB + C into a state which corresponds to (A + BC). Clearly the state of lowest energy that has a finite probability of finishing up as (A + BC) asymptotically is 2, and the probability of this ending as (A + BC) is

$$(22) \qquad \kappa_{C2} = \lim_{r\to\infty} \left\{ \int_{C2}^{C2'} |\phi_2(\rho)|^2 d\rho \Big/ \int_{-\infty}^{\infty} |\phi_2(\rho)|^2 d\rho \right\} .$$

Now, we can go from state 1 to state 2 in several ways, all of which call for energy to be supplied from an outside source, namely the translational

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N.9 For problems of this general character the minimum will always be double. For values of r less than r_J the curves will shrink to give just a single minimum, but the energy of any eigenstates of this sort of configuration will be higher than any of the states we are considering.

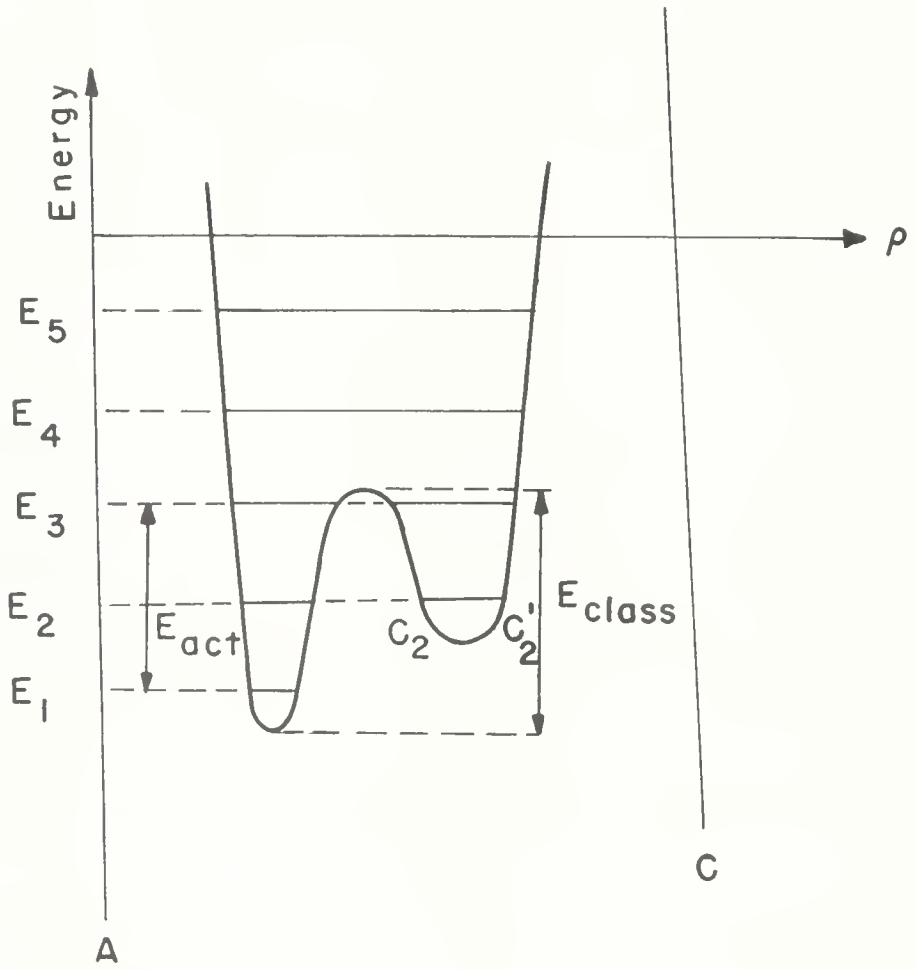

FIGURE 3

The potential $V_i^o(\rho, r_J)$, which is a section of the potential energy surface of Fig. 2 at constant r through the saddle point B*.

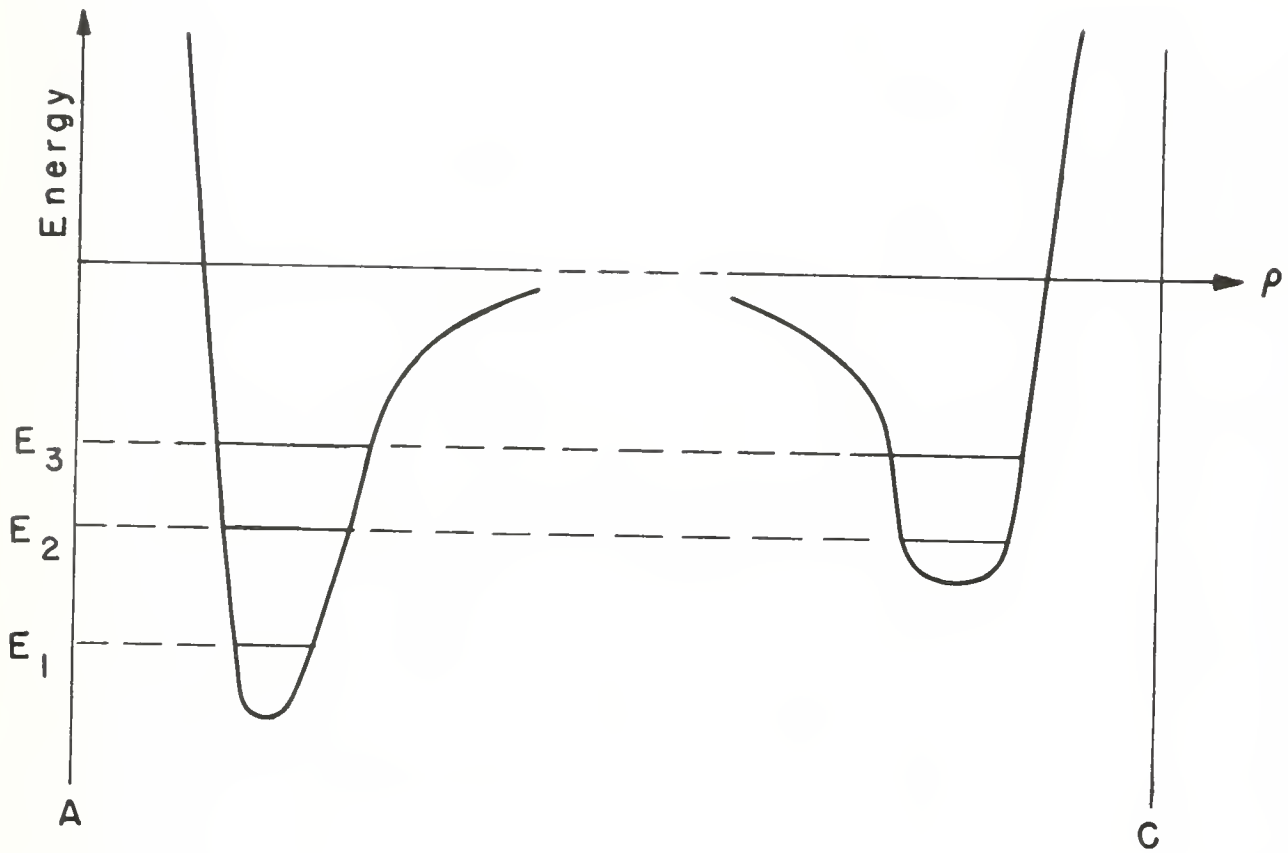

FIGURE 4

A potential $V_i^o(\rho,r')$, which is a section of the potential energy surface of Fig. 2 at constant and very large r = r'.

(thermal) motion [N.10]. The possible ways of getting from state 1 to 2 are:

(i) Excitation by an amount of energy of (E_2-E_1), and then tunnel effect until the wave function has leaked through the central barrier to such an extent that the system is in an approximation to the eigenstate 2, if this can be accomplished during one collision. In fact we know that this is not an important process, theoretically because leakage times are exceedingly long compared with collision times and experimentally because such a process would not be strongly temperature dependent for an exothermic reaction, and would give $E_{act} = (E_2-E_1)$ for an endothermic reaction. This is not observed in practice for most processes.

(ii) Excitation of state 3. We see from Figure 4 that this state is not stable as r increases, since it will presumably degenerate into either state 1 or state 2, depending on 'which side of the barrier the atom B is on during the separation'. The excess energy will go back into translation. Thus, once the state 3 is formed, there is a probability K_{C2} that we finish with the system (A + BC).

(iii) Excitation of some higher state 4,5,.. which degenerates into state 2 just the way 3 does. In fact, at reasonable temperatures $(E_4-E_3) \gg kT$, so that we may disregard these processes, since it is very unlikely that the system will have sufficient energy.

We see thus that an essential difference between the present quantum-mechanical model and the usual classical one lies in the interpretation of the activated state, and in particular of the activation energy. Classically this is the height of the saddle point above the potential at infinite separation, but in the present quantum theoretical model it is the difference between two appropriate vibrational energy levels.

N.10 We are considering an endothermic process. We could equally well consider an exothermic process by just inverting the argument.

Having now defined our model, let us ask whether a quantum treatment of this aspect of the problem is necessary in principle. The answer is quite definitely yes, because the wall is rather small, so that we have relatively few vibrational states 1,2,3,... [3]. Quantitatively, if E_{class} is the height of the central maximum above the bottom of the one-well of Figure 3, then the expression

$$(23) \qquad (1/\pi\,\hbar) \int \sqrt{2M_i\,|(E_{class} - V_i^o(\rho)|}\; d\rho$$

is of order 1-2, not 10-100, so that a quantum treatment is necessary.

6. Quantum characteristics of the rate calculation

We have discussed the character of the activated state on the present model, and have seen that it is essentially quantum-mechanical, a vibrationally excited state. Let us sketch the characteristic features of the process of formation of this state, which follows closely from earlier work on the excitation of molecular vibration by collision [5,7]:

(i) On account of the large mass of the interacting molecules, the de Broglie wavelength for the relative motion is small compared to the range d of the intermolecular potential for the states o and f:

$$(24) \qquad (\hbar\,/\,M_e\,v_n) \;=\; 1/k_n \;=\; \lambda\!\!\!^{-}_n \;\ll d; \qquad n = o,f.$$

This means that for these states we can talk of a quasi-classical orbit of the particles, and presumably do not have to use better than a WKB approximation for the wave functions; but equally we have to consider large values of angular momentum, at least up to

$$(25) \qquad \ell_1\,\hbar \;=\; k\,d\,\hbar \;\sim\; 60\,\hbar.$$

This point was not properly understood in the early work [3], and reflects the significant improvement of the more recent calculations [5,6,7].

Note that condition (24) does not apply to the state j, because essentially zero kinetic energy implies large de Broglie wavelength, regardless of the mass. This means that $\psi_j(\vec{r})$ cannot be treated in the WKB approximation, but, because condition (25) is satisfied for o- and f-states, we shall still have to consider large values of angular momentum $\ell\hbar$.

(ii) At the low energies that are of real interest here, the probability of energy transfer is small because there are many vibrations (of frequency $\omega/2\pi$) during one collision, whose average duration is of order d/v,

$$\omega \gg v/d. \tag{26}$$

(iii) To get any further, we have to make a more detailed investigation of the mechanism of energy transfer. Let us use our perturbation theory model, in which the coupling is induced by a potential V'. Classically we may speak of a definite time-dependent orbit of the incident particle, giving V' as a function of time. Then, classically, the average momentum transferred in a collision is [13]

$$\delta p = \int V' \, dt \simeq \overline{V'} \; d/v \tag{27}$$

where $\overline{V'}$ is a suitable average of V'(t) and d/v is the collision time. Now, we have

$$\delta p \; d \ll \hbar, \tag{28}$$

which is an explicit quantum condition[N.11].

[N.11] If we were to apply this argument to Coulomb interactions (disregarding the infinite range of the Coulomb potential), and put $\overline{V'} = Z\, e^2/d$, then condition (28) would just become $Z\, e^2/\hbar\, v \ll 1$.

Let us now look at conditions (i)-(iii) overall. They are clearly all independent conditions; (i) and (iii) are quantum conditions which involve Planck's constant explicitly; condition (ii) is the 'adiabatic condition' which holds both classically and quantally, and hence does not contain $\hbar$ explicitly. Thus, the characteristics of the present problem as displayed by these three conditions are the following:

Condition (i) shows that large values of angular momentum $\ell\,\hbar$ have to be taken into account.

Condition (ii) shows that the transition probability will be small, so that a careful treatment is necessary.

Condition (iii) supplements condition (i) and shows that a classical treatment of the collision is not adequate.

7. Sketch of possible methods of solution

Given some reasonable approximation to the potential energy surface, one can carry out the present sort of rate calculation with a computing machine as fast as a UNIVAC or IBM-650. The reason for this is that as we need maybe 60 values of angular momentum $\ell\,\hbar$, it is necessary to solve the radial wave equation (12e) for at least 5 values of ℓ to have something to interpolate between. This has to be done for both initial and final wave numbers, so that at least 10 translational wave functions have to be found for every point. Numerical integration of the wave equation takes about 3 minutes for one value of k and ℓ ; writing down the WKB wave function will take about one minute per point, as will the evaluation of the transition matrix element, once the wave functions are given[7]. Thus the time for computing translational matrix elements for one value of initial energy will be of the order of 30-60 minutes.

Actually the evaluation of translational wave functions and matrix elements is inherently rather well-suited to analog computing equipment. Some exploratory calculations carried out by Mr. J. P. Krawiec at AVCO show obvious advantages of analog over digital techniques. With what I understand to be excellent equipment and very good programming, the time required per matrix element (which includes finding the wave functions) will be of the order of 10-30 minutes.

On digital equipment one starts the numerical integration at the turning point of the classical motion with the values of function and derivative given by the Langer-WKB solution; the exponential decrease of the wave function for smaller distances is approximated by a WKB wave function. On analog equipment one can do much better than this in principle. The equipment is set up to produce initial and final wave functions simultaneously and to evaluate the matrix element in the same operation . The method of finding the solution is to vary the ratio of wave function to derivative at one point until one gets a solution that comes very close to zero as one integrates backwards, towards the origin. This is a very sensitive test; the equation (12e) has two linearly independent solutions, of which the regular one (which we want) goes to zero at the origin, while the irregular one diverges. Thus, if one integrates backwards, even the smallest admixture of the irregular solution will give a wave function which diverges at the origin. The sensitivity of the UNIVAC is so high that integrating backwards always gave solutions that diverged very sharply to $\pm\ \infty$; on the analog machine it has proved feasible in terms of time to search for a solution which comes quite close to zero before it diverges.

An obvious objection to analog equipment lies in the accuracy that can be obtained; the results obtained are reproducible to better than $1^{o}/o$ for the matrix element, and the absolute accuracy of the matrix elements is estimated as within $5^{o}/o$. I feel that $5\text{-}10^{o}/o$ error is about the maximum that can be tolerated in the matrix element, not so much in terms of the accuracy of the final numerical results, as that if the total cross section is uncertain by more

than 10-20^{o}/o it will be very hard to draw any conclusion from one's results.

In addition to the translational matrix elements, one also has to find the internal wave functions $\phi_n(\rho)$ and their matrix elements. This is not a major problem because it just has to be done once for the whole calculation.

8. The effect of rotation[N.12]

In the present analysis we have considered only collinear collisions of the three particles A, B, C. This is a simplification which is almost always made in the statistical calculations [1,2] N.1. In practice, we shall find that most actual collisions occur at an angle rather than head-on, and so the effect of rotational motion of the AB-molecule should be considered in any quantitative calculation. This will lead to the following differences:

(i) Conservation of angular momentum will no longer be just

$$\ell_n = \ell_{n'} , \tag{14}$$

as has been considered in the preceding, but

$$\vec{L}_n + \vec{J}_n = \vec{L}_{n'} + \vec{J}_{n'} , \tag{29}$$

where $\vec{L}$ is the orbital angular momentum in the $\vec{r}$-motion, having the eigenvalue $\hbar\sqrt{\ell(\ell+1)}$, while $\vec{J}$ is the angular momentum of rotation of the AB-molecule, i.e., in the $\vec{\rho}$-motion. Its eigenvalues will be $\hbar\sqrt{j(j+1)}$.

(ii) There will be a potential energy surface for each possible combination $(j_o\text{-}j_f)$, i.e., for each initial and final state of rotation in the ρ-coordinate. Thus there will be a corresponding change in the condition for conservation of energy, (13), in that $\epsilon_n = \epsilon_n(v_n, j_n)$, where v_n and j_n are respectively vibrational and rotational quantum numbers.

N.12 This section was written as a result of some remarks by Dr. S.H. Bauer.

(iii) Precisely which transitions j_o-j_f are possible depends on the form of $V_i^o(\rho)$, and more particularly on $V'(\vec{\rho},\vec{r})$. If V_i^o is independent of α, β, the polar coordinates in the $\vec{\rho}$-coordinates, we have,

$$\phi_n(\vec{\rho}) = \phi_n(\rho)\, Y_{j,m}(\alpha,\beta); \tag{30}$$

where $Y_{j,m}$ are normalized spherical harmonics. Then if V' is independent of (α,β), $j_o = j_f$; if $V' \sim \cos\alpha$, $j_o = j_f \pm 1$, etc.

(iv) Overall, the effect of molecular rotation on the vibrational motion will be the addition of rotational fine structure to the energy level diagrams. However, this does not invalidate any of the present arguments regarding the character and magnitude of quantum jumps, because of the selection rules that will be enforced by a 'reasonable' form of V'. One will presumably have to make a number of calculations like the present one, rather than take combinations of possible transition matrix elements within each calculation.

9. Discussion

In the preceding analysis the problem of calculating reaction rates has been examined; we see that it is a very difficult problem. Among other things, we have seen that the customary statistical theory is inadequate in many respects. Yet it is perfectly reasonable for a chemist, who is familiar with the statistical theory and knows its successes, to say that I admit that I cannot yet make quantitative calculations of reaction rates, yet I object to the statistical theory which does make quantitative predictions. Or, to put it another way, why does the (supposedly inadequate) statistical theory give sensible results?

The answer to this has several aspects. First, the statistical theory works at the phenomenological level of explaining qualitatively the meaning

of the two parameters E_{act} and P_{fo} in the expression (2) for the reaction rate $k_{fo}(T)$, and consequently of correlating E_{act} and P_{fo} values for different reactions. It is clear that once one knows the E- and P-values for a number of reactions, one can go a fair distance towards interpolating rates of related processes, or even making moderate extrapolations; but if there is no information that bears on a given sort of reaction, or if simple correlations do not give the correct result, it is necessary to go to some deeper theory, such as the present one.

Furthermore, once we have a potential energy surface for a given reaction, it will be possible to use both the classical, statistical theory and the present quantum-mechanical theory to predict E- and P-values. These values will evidently be different on account of the different models used, but to make a comparison between the two theories that can be compared with experiment we should need very much better potential energy functions than are available at present (cf. Section 3).

In conclusion, one can paraphrase the conclusion of a related piece of work [7]. At present the chief obstacle to the quantitative calculation of reaction rates is the lack of detailed and accurate potential energy functions. Once this is overcome for specific processes, it should be possible to make rather accurate and detailed calculations of reaction rates. This will call for considerable effort, though very much less than is involved in obtaining potential energy surfaces. The statistical theory will certainly remain useful at the empirical level outlined above, though for certain elementary and crucial reactions such as (16a,b), the present method may well be the only way of getting reliable theoretical answers.

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References

[1] Fowler, R.H. and Guggenheim, E.A. - Statistical Thermodynamics; Cambridge Univ. Press, 1939, Ch. 12.

[2] Eyring, H., Walker, J. and Kimball, G.E. - Quantum Chemistry; New York, John Wiley, 1944, Ch. 16.

[3] Bauer, E. and Wu, Ta-You - Quantum-mechanical calculation of reaction rates; J. Chem. Phys., 21, 726, 2072L (1953).

[4] Mott, N.F. and Massey, H.S.W. - Theory of Atomic Collisions, 2nd Ed.; New York, Oxford Univ. Press, 1949, p. 294.

[5] Bauer, E. - Method of calculating cross sections for molecular collisions; J. Chem. Phys., 23, 1087 (1955). Also N.Y.U., Inst. Math. Sci., Div. of EM Res., Research Report No. CX-17, Oct., 1954.

[6] Widom, B. - Inelastic molecular collisions with a Maxwellian interaction energy; J Chem. Phys.; 27 940 (1957).

[7] Salkoff, M. and Bauer, E. - Excitation of molecular vibration by collisions;N.Y.U., Inst.Math.Sci.,Div. of EM Res.,Res. Report No.CX-31, July,1957. See also Bull.APS,ser.II,2 No.4,Abstract QA1. To appear in J.Chem. Phys.

[8] Whittaker, E.T. - Analytical Dynamics; Camb. Univ.Press, 1937, p. 348.

[9] - Reference 7, ch. 3.

[10] Gombas, P. - Das Mehrteilchenproblem in der Wellenmechanik; Basel, Birkhäuser, 1950.

[11] James, H.M. and Coolidge, H.S. - Energy of the hydrogen molecule; J. Chem. Phys. 1, 825 (1933); 3, 129 (1935).

[12] Schiff, I. - Quantum Mechanics; New York, McGraw-Hill, 1949, ch. 8.

[13] Williams, E.J. - Space-time concepts in collision problems; Rev. Mod. Physics; 17, 217 (1945).